

THE IMPROVEMENT OF ZINC ELECTRODES FOR ELECTROCHEMICAL CELLS

by
J.E.OXLEY

FACILITY FORM 602

N 67-30067

(ACCESSION NUMBER)

(THRU)

40

(PAGES)

1

(CODE)

CE-85251

(NASA CR OR TMX OR AD NUMBER)

03

(CATEGORY)

LIBRARY COPY

JAN 25 1967

MANNEO SPACE FLIGHT CENTER
HOUSTON, TEXAS

FINAL REPORT

JUNE 12, 1964 — MARCH 24, 1965

Revised

prepared for

GODDARD SPACE FLIGHT CENTER

CONTRACT NAS 5-3908

LEESONA MOOS LABORATORIES

GREAT NECK, NEW YORK

THE IMPROVEMENT OF ZINC ELECTRODES
FOR ELECTROCHEMICAL CELLS

BY

J. E. OXLEY

FINAL REPORT

JUNE 12, 1964 - MARCH 24, 1965

prepared for
GODDARD SPACE FLIGHT CENTER
CONTRACT NAS 5-3908

APPROVED BY:

A handwritten signature in dark ink, appearing to read 'H. G. Oswin', is written over a horizontal line.

H. G. Oswin
Manager - Chemistry Department

LEESONA MOOS LABORATORIES
GREAT' NECK, NEW YORK

ABSTRACT

This is the final report on Contract NAS 5-3908 for "The Improvement of Zinc Electrodes for Electrochemical Cells". The work carried out during the entire program is summarized and a review is provided of other work in this and related areas.

The requirement for higher energy outputs per unit weight of battery in advanced space missions has pointed out the need for developing the Ag/Zn battery into a more reliable, rechargeable battery. Although present Ag/Zn batteries when used as a primary battery (i. e., single discharge), are capable of yielding up to 90 watt hours per pound, in practice it has been found that for use as secondary batteries capable of sustaining hundreds of charge/recharge cycles, only 30 watt hours per pound can be achieved.

The major obstacle which presently prevents an improvement beyond this figure for the Ag/Zn secondary battery is the deterioration of the zinc electrode which occurs during recharging by the formation of dendrites on the Zn negative plate. These dendrites are associated with the fact that zinc is quite soluble in the electrolyte, and that during the charging and discharging of Zn electrodes, extensive rearrangements of the Zn physical form occur.

An exploratory research program has been conducted with the objective of defining the nature of the problem as exactly as possible and indicating the directions in which improvements of this system should be sought.

Our understanding of the problem has advanced significantly. Two main parameters which control dendrite growth have been identified. These are: (1) the overpotential which governs the morphology, and (2) the rate and type of zincate diffusion (i. e., spherical or linear) in relation to the geometry of the electrode/electrolyte interface, which controls both the overall growth rate and the selective propagation of individual dendrites.

It was shown that density differences between zincate and potassium hydroxide, and hydrogen bubble formation both lead to local convection and thereby enhanced propagation.

Two remedies were suggested which are expected to provide improvements in the cycle life of silver/zinc batteries. These are: (1) the

use of intermittent charging which was shown to produce a denser and more even deposit, and (2) a method for elimination of preferential edge growth.

Finally, a program of further work in this area is suggested.

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
	Abstract	ii
I	Introduction	1
II	Discussion	5
2.1	Experimental Methods	5
2.2	Experimental Results	8
III	New Technology	26
IV	Conclusions and Recommendations	27
	Appendix	31
	References	33

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Recessed Electrode Holder	7
2	Capillary Diffusion Apparatus	9
3	Progressive Stages in Thickening of the Diffusion Layer at a Rough Surface	16
4	Dendrite Growth at $-1.8V$	18
5	Cross-Section Photomicrographs	19
6	"Single" Dendrites	21
7	Mossy Dendrite Growth at $-1.65V$	23
8	Dendrite Growth on Amalgamated Electrode	24
A-1	Potential Series for Silver/Zinc Battery	32

SECTION I - INTRODUCTION

The growth of zinc dendrites during the charging of silver/zinc batteries is an undesirable feature of this and other systems employing zinc viz. zinc/air and nickel/zinc and threatens to outweigh the advantage of high power to weight and volume ratio which zinc otherwise imparts.

Dendrite growth is responsible for early failure due to shorting, loss of capacity due to breakaway of active material from the negative plate and, therefore, variability of performance and limited cycle life. Although it can be argued⁽¹⁾ that the poor cycle life of silver/zinc batteries can be ascribed to separator deficiencies, it is likewise evident that early separator failure would not occur but for the growth of zinc dendrites.

The problem of zinc dendrite growth has not received wide attention in spite of its evident importance and only a few attempts notably by Higgins and Bruins⁽²⁾ have been made to define the mechanism of either initiation or propagation. These authors discussed the role of diffusion and also examined the effect of adding aluminum hydroxide as a means of reducing zincate solubility.

A number of practical remedies have been proposed. Kryukova⁽³⁾ has shown that dendrite growth is inhibited in cellulose-based polymer films which have been treated with surfactants. Such materials are adsorbed preferentially on the tip of a dendrite advancing into the film and thereby promote side-branching (which is of course the preferred alternative to linear dendrite propagation). Attempts to reduce propagation by dissolving the same surfactants in the electrolyte were unsuccessful. Kryukova also noted that dendrite propagation through the cellulose films was retarded by increasing temperature.

A useful discussion of the action of leveling agents, e. g., coumarin and thiourea in electrodeposition was published recently by Kudryavtsev and co-workers.⁽⁴⁾ The various theories for the preferential adsorption of surfactants at surface asperities were reviewed.

Romanov,⁽⁵⁾ who is the author of a large number of papers on the subject of secondary batteries, has described the use of alternating current techniques for charging silver/zinc and nickel/zinc batteries. He claimed⁽⁶⁾ that dendrite formation is avoided when the battery is charged with asymmetric AC of frequency between 50 and 200 cycles.

Romanov was also able to double the cycle life of nickel/zinc batteries by wrapping the ends of the zinc electrodes with an alkali resistant film such as polyethylene.⁽⁷⁾ He had previously observed that shorting usually occurred at the edges of the electrodes. This was ascribed to the current distribution and to the presence of free zincate at the edges.

Additions to the electrolyte or to the zinc electrode have been extensively tried, but mainly by investigators in the plating industry and many claims exist for the bright plating of zinc from alkaline solutions containing for example cyanide,⁽⁸⁾ tin,⁽⁹⁾ and lead.⁽¹⁰⁾ As stated above in reference to Kryukova's work, organic additives to the electrolyte have not had any beneficial effects in silver/zinc batteries. It should be born in mind that any additive must be compatible with the overall operation of the battery. For example, cyanides have been repeatedly used as leveling agents but they would clearly have a deleterious effect on the silver electrode, causing complexing and dissolution.

More basic studies have been carried out by Barton and Bockris⁽¹¹⁾ who studied the growth of silver dendrites in molten nitrates. They proposed a theory for dendrite propagation in terms of diffusion. The higher rate of growth at the tip of a dendrite was shown to be due primarily to the onset of spherical, as opposed to linear diffusion. Under given conditions of concentration and surface activity, the former gives rise to the largest net flux per unit area. This may be clarified in terms of the Nernst diffusion layer concept;⁽¹²⁾ the thickness of the diffusion layer is lowest at the points where the radius of curvature is smallest, which are also farthest removed from the substrate. Thus, once a situation has been created where surface asperities or protrusions exist, the growth of such irregularities will be accelerated by the normal processes of convective diffusion. This theory has found particular relevance in the present study and is the subject of most of the work carried out during the third quarter of this contract.

Wranglen⁽¹³⁾ has given a useful descriptive treatment of dendrite formation in terms of space lattice parameters for lead, silver, tin, and cadmium electrodeposition from aqueous solutions. Such an analysis has not been attempted in the present work, but should probably be included in a future study.

Work has been directed under the present contract to identify the mechanism and possible means of elimination or mitigation of the effects of dendrite growth. The approach adopted has been to conduct an electrochemical analysis of the zinc/zincate couple. The initial phase of this study (Quarterly Report No. 1), was devoted to

obtaining current-voltage curves for both the anode and cathode processes under a variety of conditions of concentration of potassium hydroxide and dissolved zincate. In addition, general observations were recorded of the different dendrite morphologies. The main conclusion from this work was that the principal parameter controlling dendrite morphology is the overpotential. A definite trend in dendritic form from "mossy" to "acicular" was apparent as the potential of growth was made more cathodic to the reversible potential of the zinc/zincate couple. In more recent work it became apparent that a secondary parameter which controls the dendrite morphology is the extent to which the rate of deposition is controlled by mass transfer and the geometry of the electrode/electrolyte interface. Further observations of interest were that during anodic dissolution: (1) a highly active zinc surface is formed that is capable of displacing hydrogen from the electrolyte much more rapidly than does smooth zinc, and (2) most of the current during dissolution goes toward reducing the thickness of the individual dendrites, rather than reducing the length.

During the second quarter dendrite propagation rates were measured. The rate of propagation, which was measured in terms of mm/coulomb, is clearly a significant parameter in determining the tendency for dendrites to cause shorting and was shown to increase with increasing overpotential. At the more cathodic potentials the real rate was masked by the simultaneous evolution of hydrogen and the measured propagation rate was therefore less at -1950 mV than -1850 mV. Metallographic cross-section studies were carried out with the aim of identifying the origin of dendrite nucleation and the processes which occur during the early stages of growth (initiation). Although no certain analysis was possible, a tentative conclusion was that the number of dendrites nucleated may be related to the frequency of defect sites. It was also noted that of the dendrites which were nucleated, only a small percentage grew to a size $>0.001''$. The role of diffusion was discussed and its importance was illustrated with reference to dendrite propagation rates, growth through separator materials, edge effects and densification.

During the final quarter the principal aim has been to define more exactly the role of diffusion in this system. This necessitated a separate polarographic determination of the diffusion coefficient of the zincate ion in KOH. The role of diffusion in determining the rate of dendrite propagation and in certain instances dendrite morphology has been demonstrated. Two remedies for existing causes of failure are proposed, both of which rely upon an understanding of the mass transfer in this system.

In a parallel study on zinc dendrite formation which is being conducted at Yardney Electric Corporation⁽¹⁴⁾ it has been shown that rotation of the electrode causes the formation of a smooth deposit as judged both visually and by the fact that the current, at a fixed potential, does not rise appreciably with time. Two alternate explanations for this result can be offered at this moment:

- a. That rotation causes complete elimination of concentration polarization, and that under such conditions no dendrite formation occurs. This conclusion is favored by Yardney and is supported by the fact that the calculated diffusion limited current was much higher than that actually observed. This is nevertheless surprising in view of: (1) the relatively low speed of electrode rotation (1440 rpm), (2) the fact that the reduction of zincate is an intrinsically rapid (i. e., reversible) process, and (3) even at potentials very close to the reversible potential where the process is certainly activation controlled, a smooth deposit is not obtained in the absence of rotation.
- b. That rotation causes the diffusion layer to be very small with respect to the surface irregularities or protrusions which would eventually lead to dendrite growth (cf. Barton and Bockris⁽¹¹⁾). Under the latter conditions, since the diffusion layer follows the contours of the surface there can be no preferred sites for dendrite propagation. This seems to be the more probable explanation.

Some analogous experiments have been performed in the present work but instead of maximizing convection, the opposite was effected by electrodepositing zinc from a zincate solution within a capillary, thereby maintaining conditions of semi-infinite linear diffusion. Such conditions approximate those existing in a silver/zinc battery. This technique has also served to indicate the role of hydrogen bubble formation in causing local convection and also the relative rates of propagation of a dendrite and the thickening of the diffusion layer.

No real progress has been made in understanding the cause of initiation of dendrites. Some experiments have been carried out comparing growth on annealed and cold-worked samples of zinc but they were rather inconclusive.

SECTION II - DISCUSSION

2.1 EXPERIMENTAL METHODS

2.1.1 Materials

No change has been made in source of ZnO, Zn and KOH which were employed in the first two quarters.

The following additives to the electrolyte have been tried:

- a. Tetramethylammonium hydroxide pentahydrate (C. P. grade K & K)
- b. Tin as Sn^{++} (Fisher, certified 99.6%)
- c. Thiourea (Baker, analyzed 99.6%)
- d. Ethylenediamine (Fisher, certified 100%)

Experiments have been carried out using amalgamated electrodes. These were prepared using a solution containing 33.3 g HgCl_2 and 8.3 g KBr in 1000 ml H_2O . The zinc electrodes were washed in methyl alcohol, air dried and immersed for 40 seconds in the solution.

2.1.2 Equipment and Apparatus

2.1.2.1 Cell and Propagation Rate Measurement

The cell for dendrite growth was the same as used in the previous quarter. A change was, however, made in the technique for measuring propagation rates. Previously photographs were taken of a growing dendrite and the extent of propagation determined from a comparison with a standard grid, the same section of the electrode surface being observed throughout a given growth. A more direct method has since been used in which the electrode is attached to a stage which is moveable upwards or downwards with a micrometer head. A brass semicircular disc was inserted into the telemicroscope at the point of focus and served as the point of reference. In operation, the electrode was brought to a point even with the point of reference and its position was read on the micrometer. As

the dendrites grew, the electrode was lowered to keep the leading edge of the growth at the reference point. The difference in the vernier readings was the extent of propagation and this was accurate to $\pm 0.001''$, which amounts to $\pm 5\%$ of an 0.5 mm growth.

2. 1. 2. 2 Electrode Construction

It was pointed out in the second quarterly report that the observed rate of dendrite propagation is greater at the edges than in the center of the electrode. This was explained in terms of the geometry of the electrode/electrolyte interface and the fact that growth at the edges is controlled by spherical diffusion. Clearly, the preferential growth of dendrites at the edges of an electrode renders the measurement of propagation at the center uncertain and therefore most of the propagation experiments during the past quarter have been carried out with a recessed electrode as shown in Figure 1. The depth of recession was 0.020" which is approximately the separation of the plates in a silver/zinc battery. With such an electrode, preferential edge growth was eliminated until the dendrite had grown to a height of 0.020". This is further discussed below with particular reference to the elimination of edge effects of silver/zinc batteries.

2. 1. 2. 3 Polarography

Polarography was selected as being the quickest and most reliable method available for determination of the diffusion coefficient of zincate in 44% KOH. Polarograms were obtained using a Sargent model XV polarograph in conjunction with a dropping mercury electrode. The diffusion coefficient was calculated from the Ilkovic equation:⁽¹⁵⁾

$$i_d = 607 n D^{1/2} C m^{2/3} t^{1/6}$$

where i_d is the average current during the life of a drop in μA , n is the number of electrons transferred, D is the diffusion coefficient in cm^2/sec , C is the concentration in moles/ cm^3 , m is the rate of flow of mercury from the dropping mercury electrode capillary in mg/sec and t is the drop time in seconds, other parameters have their usual meaning.

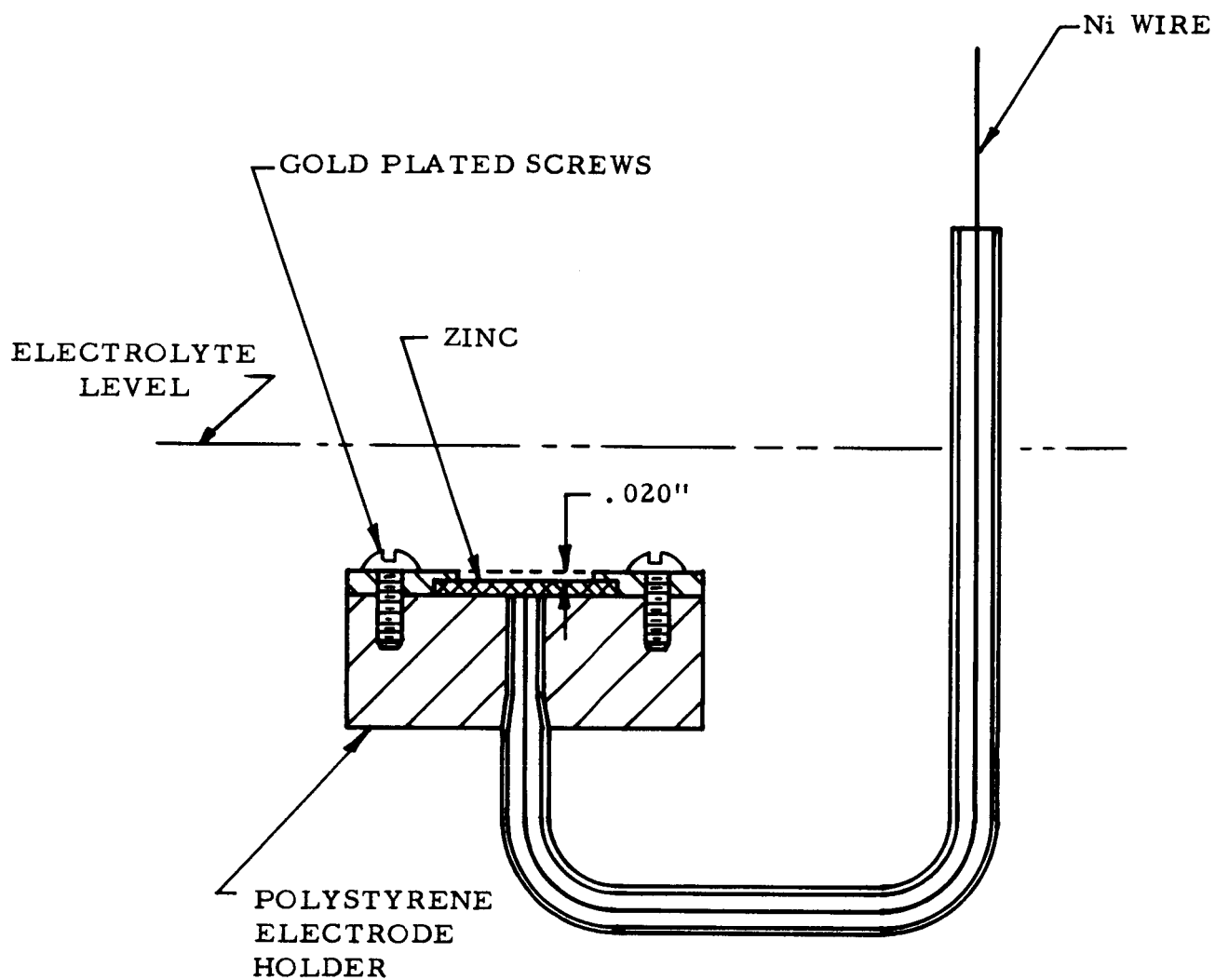


Figure 1. Recessed Electrode Holder

The drop rate and drop time were determined according to established procedures.⁽¹⁵⁾

2. 1. 2. 4 Capillary Diffusion Experiments

It is clear from what has been discussed previously in reference to the theory for dendrite propagation that the addition of a convective component to the mass transfer will have a strong influence upon the diffusion profile surrounding the zinc cathode, and therefore upon the growth characteristics. Such a situation was artificially created in the experiments of Yardney by using a rotating disc electrode. A situation where exactly the opposite occurs can also be created by carrying out the electrodeposition within a capillary whereby convection is eliminated and the reaction becomes entirely governed by semi-infinite linear diffusion. This method was developed by Laitinen and Kolthoff.⁽¹⁶⁾

Figure 2 shows a diagram of the apparatus used. Experiments were carried out using three different concentrations of zincate. The current at a fixed potential of -1.8 volt versus SCE was recorded as a function of time. At the start of each run the electrode was ground smooth and amalgamated. Three different electrode/electrolyte configurations were studied:

- a. with the diffusion path downwards,
- b. with the diffusion path upwards (with respect to force of gravity), and
- c. with the diffusion path at angle (10°) to the vertical.

2. 2 EXPERIMENTAL RESULTS

2. 2. 1 Polarographic Determination of the Diffusion Coefficient of Zincate in 44% KOH

The diffusion coefficient (D) of zincate in 1N NaOH is known⁽¹⁷⁾ and, on the basis of this value and the fact that the diffusion coefficient varies inversely with viscosity, an estimate was made on the value in 44% KOH (see Quarterly Report No. 2, page 19). This estimate was $1.3 \times 10^{-6} \text{ cm}^2/\text{sec}$. Using the equation

$$i = n FCD/\delta \tag{1}$$

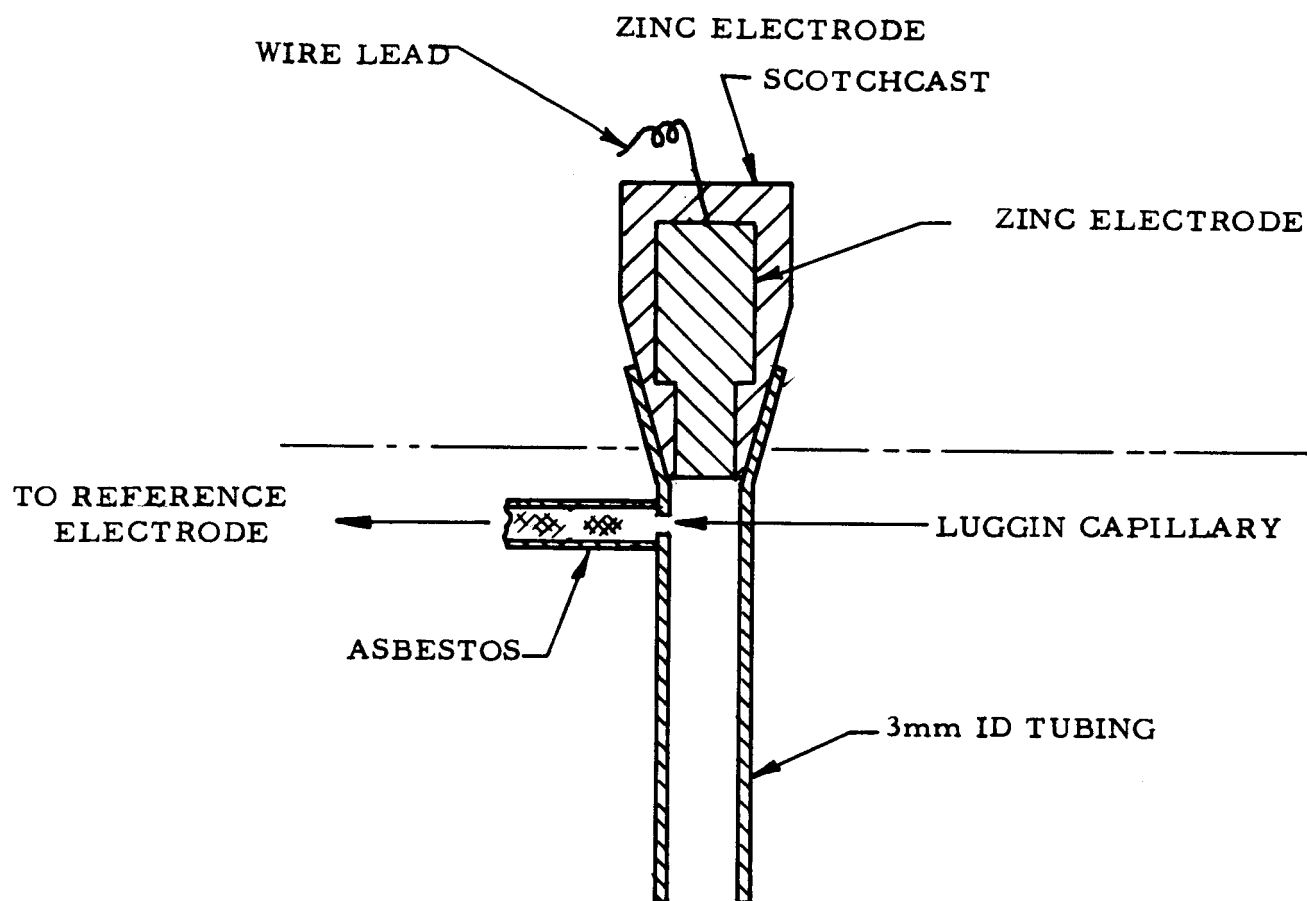


Figure 2. Capillary Diffusion Apparatus

where i is the current density in amp/cm², n is the number of electrons transferred, F is the Faraday, C is the concentration in moles/cc, D is the diffusion coefficient in cm²/sec and δ is the diffusion layer thickness in cm, a rough calculation of the expected limiting current for a saturated solution of zincate, using the admittedly arbitrary value of 5×10^{-2} cm for the diffusion layer thickness, led to a value of 5 mA/cm². This is considerably smaller than the currents which are actually observed (50 mA/cm²). This discrepancy is difficult to explain on the basis of surface roughness alone, since the figure of 50 mA/cm² was obtained after two or three minutes when the extent of dendrite growth is considerably less than the assumed diffusion layer thickness (5×10^{-2} cm). Therefore, in view of this uncertainty and the evident importance of diffusion in this system, it was decided to measure the diffusion coefficient of zincate in 44% KOH directly using polarography.

The value of D was first determined in 1N NaOH and a value in fair agreement with that reported by Lingane⁽¹⁷⁾ was found. Following this, a determination was made in 1N KOH. Surprisingly, the value obtained differed from that found in 1N NaOH in spite of the small difference in the viscosity of the two solutions. Finally, a measurement was made in 44% KOH and a value of 1.8×10^{-6} cm²/sec was found, which agrees quite well with that estimated earlier.

The polarographic results obtained are summarized in Table 1. Included in this table are the half-wave potentials for zincate reduction and the potentials for the decomposition of the supporting electrolyte. The latter process is the reduction of potassium ions and, as expected, takes place at a considerably less cathodic potential in the higher concentration of KOH. The reduction of the potassium ion proceeds at measurable rates at about 1 volt from the reversible potential owing to the solubility of potassium in mercury and the consequent maintenance of low potassium activity.

Since the value for D obtained in the present work differs only slightly from that estimated earlier (Quarterly Report No. 2), it follows that the value assumed previously for the diffusion layer thickness (5×10^{-2} cm) and used to estimate the limiting current is in error and that the actual thickness is far less than this. The small diffusion layer thickness is probably a result of convection at the electrode/electrolyte interface caused by hydrogen bubble formation.

Table 1. Polarographic Data

System	Diffusion Coefficient D in cm ² /sec	Electrolyte Decomposition Potential -Volts vs. S.C.E.	i d μA	E _{1/2} volts vs. S.C.E.	m mg/sec	t sec/drop
10 ⁻³ M ZnO in 1M NaOH	6.0 x 10 ⁻⁶	-1.92	4.1	1.51	1.2	3.4
ZnO in 1M NaOH (Lingane)	6.7 x 10 ⁻⁶	--	-	1.53	-	-
10 ⁻³ M ZnO in 1M KOH	2.1 x 10 ⁻⁵	-1.94	8.0	1.54	1.3	3.0
2 x 10 ⁻² M ZnO in 44% KOH	1.8 x 10 ⁻⁶	-1.80	56	1.73	1.88	2.2

2. 2. 2 Electroreduction of Zincate Within a Capillary

These experiments were carried out in an attempt to learn whether, (a) dendrite propagation and/or (b) different dendrite morphologies are in any way governed by the incidence of spherical diffusion. In addition, it was intended to demonstrate how far the normal diffusion laws are obeyed during the deposition of zinc from a saturated zincate solution.

The equation

$$i = n F C \sqrt{\frac{D}{\pi t}} \quad (2)$$

gives the relationship between current i in A/cm^2 and time, t , in seconds at a fixed potential in the diffusion limited region. The parameters n, F, C and D are in the same units as for equation (1).

From equations (1) and (2)

$$\delta = \sqrt{D \pi t} \quad (3)$$

Equation (3) shows that the rate of growth of the diffusion layer should be governed only by the diffusion coefficient D .

Any departure from equation (2) should be related to either:

- a. density gradients which cause natural convection
- b. local convection at the electrode/electrolyte interface brought about by gas bubbles (H_2)
- c. a faster rate of growth of electrodeposited zinc than the rate of extension of the diffusion layer

The presence of a cellophane separator in a silver/zinc battery also has the effect of excluding convection and, with the reservation that the diffusion coefficient of zincate in cellophane is considerably less than in the free electrolyte, it is felt that this approach is particularly relevant to an actual silver/zinc battery.

The first series of experiments were carried out with the diffusion path downwards, i. e., in the same direction as the force of gravity. Equation (2) was not obeyed and in fact the current was found to rise instead of decrease with time. This result indicated that the diffusion layer did not thicken with time as would be expected from equation (3). Instead, as the surface became rougher (as a result of dendrite formation) the current likewise increased since the diffusion layer thickness, being small compared to the surface irregularities, caused the flux of zincate to be governed by the real electrode area. This effect is attributed to natural convection which results from density differences between potassium hydroxide and zincate solutions, the latter being the more dense. Natural convection will occur when the direction of diffusion is such that the less dense solution lies below the denser solution.

The above interpretation was confirmed by the second series of experiments in which the diffusion path was upwards. Experiments were run at three different concentrations of zincate; 1.13M (saturated solution), 0.1M, and 0.02M. The current was found to decrease with time for all three concentrations. Furthermore, it was seen to be approximately constant (as demanded by equation (2)) during the initial stages of electrolysis which permitted a calculation of the diffusion coefficient (D). Values were obtained which were close to that found polarographically. The values were 1.7×10^{-6} , 1.7×10^{-6} , and 1.3×10^{-6} cm²/sec for the 1.13, 0.1 and 0.02M solutions respectively. However, departures from equation (2) were observed after longer periods of electrolysis and these were attributed to convection which results from bubble formation at the electrode surface. This was not entirely eliminated by amalgamation. This is consistent with the finding of larger currents when deposition was carried out on an unamalgamated electrode. One would expect the influence of convection on the diffusion layer thickness to be most marked at the higher concentrations of zincate where dendrite growth is fastest and this was found to be the case. Table 2 summarizes the results which were obtained in these experiments. It is considered that the most significant aspect of these capillary diffusion experiments is the effect of density differences.

When the capillary was arranged at an angle of 10° to the vertical, dendrite growth predominated at the lowest point of the electrode. In the saturated solution the rate of propagation at this point was about ten times greater than elsewhere. Such a large effect was not found when electrolysis was carried out in the free electrolyte owing to the stronger influence of forced convection. In the latter case, it was nevertheless found that the deposit was more even and exhibited less

Table 2. Capillary Diffusion Data

Concentration of Zincate (molar)	Equation (2) Obeyed Approximately (seconds)	Diffusion Layer Thickness (δ) After Time In Previous Column (cm)	Current fell for (seconds)	Diffusion Coefficient D (cm^2/sec)
1.13	65	1.9×10^{-2}	~ 200	1.7×10^{-6}
0.1	120	2.5×10^{-2}	> 1000	1.7×10^{-6}
0.02	400	4.8×10^{-2}	> 1000	1.3×10^{-6}

tendency for individual dendrite propagation on the underside of a horizontally arranged electrode. No quantitative data or photographs are available for this effect.

Such effects are clearly of relevance in analyzing the possible influence of gravity, and further work is recommended in this area.

2. 2. 3 Induction Period for Dendrite Propagation and Intermittent Charging

In the studies of the growth of silver dendrites from molten salts, Barton and Bockris⁽¹¹⁾ reported an induction period for dendrite propagation of several minutes. This was ascribed to the fact that a growing protrusion or prismatic outgrowth has to penetrate the diffusion layer before true dendritic growth can begin. Such a proposition is not unreasonable and is illustrated in Figures 3(a), 3(b), and 3(c), which represent the progressive stages in the growth of the diffusion layer after current starts to flow at some potential in the limiting current region. This diagram shows the different diffusion profiles which are established. In the absence of convection, the diffusion layer thickness is governed by equation (3). As an example, in the present system where the diffusion coefficient has been determined to be 1.8×10^{-6} cm²/sec; the diffusion layer thickness is equal to 1.8×10^{-2} cm after the current has flowed for one minute and is equal to 2.6×10^{-2} cm after two minutes. If a certain roughness is assumed at the beginning of electrolysis, then it can be seen that initially the diffusion layer is small compared to the surface irregularities as shown on Figure 3(a). Under such conditions, the flux of zincate to the electrode is evenly distributed over the entire surface and growth should be even. Subsequently (see Figure 3(b)), the diffusion layer grows such that its thickness is of the same order of magnitude as the surface irregularities and under these conditions there is less tendency for the diffusion layer to follow the exact contours of the surface, therefore, the largest asperities will have the most ready supply of zincate and will grow most rapidly. Eventually, if convection can be entirely eliminated, the diffusion layer becomes greater than the dimensions of the surface irregularities (as shown in Figure 3(c)), and the preferential propagation (at any rate by diffusion) of individual dendrites should be eliminated entirely. However, such a condition cannot exist in this system because of natural convection which results from density differences and local forced convection brought about by hydrogen bubble formation.

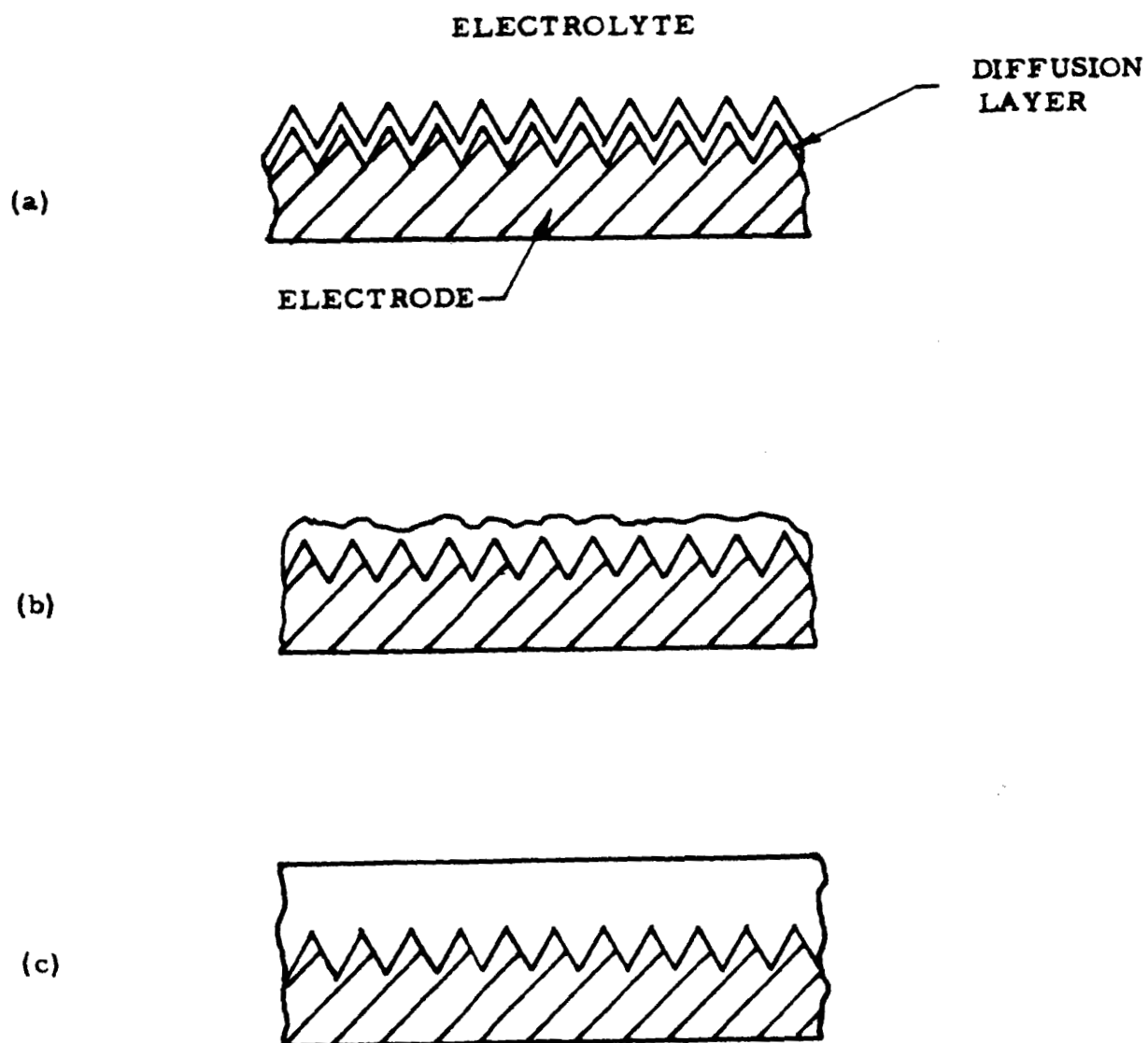


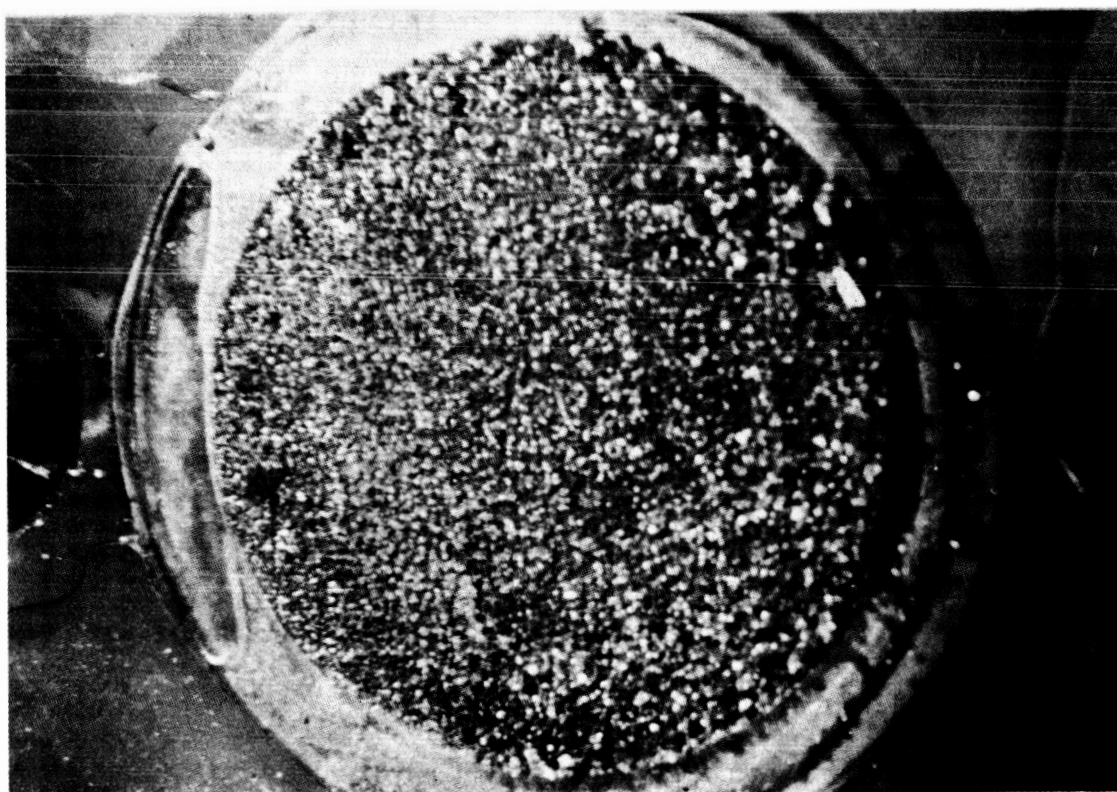
Figure 3. Progressive Stages in Thickening of the Diffusion Layer at a Rough Surface

The above theoretical considerations prompted a study of the possible usefulness of intermittent charging as a means for promoting the even deposition of zinc. A series of intermittent charging experiments were carried out in which the "on" period was 45 seconds and the "off" period was 2 minutes. The duration of the "on" period was selected to correspond approximately to the interval during which, according to the above theory, the diffusion layer thickness is still small compared to surface irregularities. The "off" period was made long enough (again approximately) to allow decay of the concentration gradient built up during the "on" period. These experiments were quite successful and indicated the possibility of employing such a method in the actual charging procedure of silver/zinc batteries.

Figures 4(a) and 4(b) show the deposits obtained by on/off charging and by continuous charging. The significant feature is the relative smoothness of the deposit obtained by on/off charging. Propagation rates were also determined and it was seen that with on/off charging, the rate was only about one-third that with continuous charging (for the same total number of coulombs passed). Deposition was carried out at -1.8 volt and, although it is not very clear from Figure 4, it did seem that the on/off charging gave a more mossy deposit. This was confirmed by a metallographic cross-section examination of the growth (see Figures 5(a) and 5(b)). In contrast with the experiments described in the second quarterly report (page 10), where it was shown that continuous charging leads to the extensive propagation of only a few dendrites (with most remaining $< 0.001''$), on/off charging leads to a more even growth over the entire surface. This is clearly a most desirable feature and illustrates both the general validity of the theoretical considerations above and that this is possibly an advantageous technique for charging batteries. The times selected for these experiments viz. 45 seconds "on" and 2 minutes "off" were arbitrary and would probably not be appropriate when a cellophane separator is present; but the same theory would apply. When charging is carried out at constant current, polarization will be low during the initial stages of charging before the diffusion layer thickens and consequently the more desirable, mossy growth should be obtained. Further work in this area should demonstrate preferred recharging techniques.

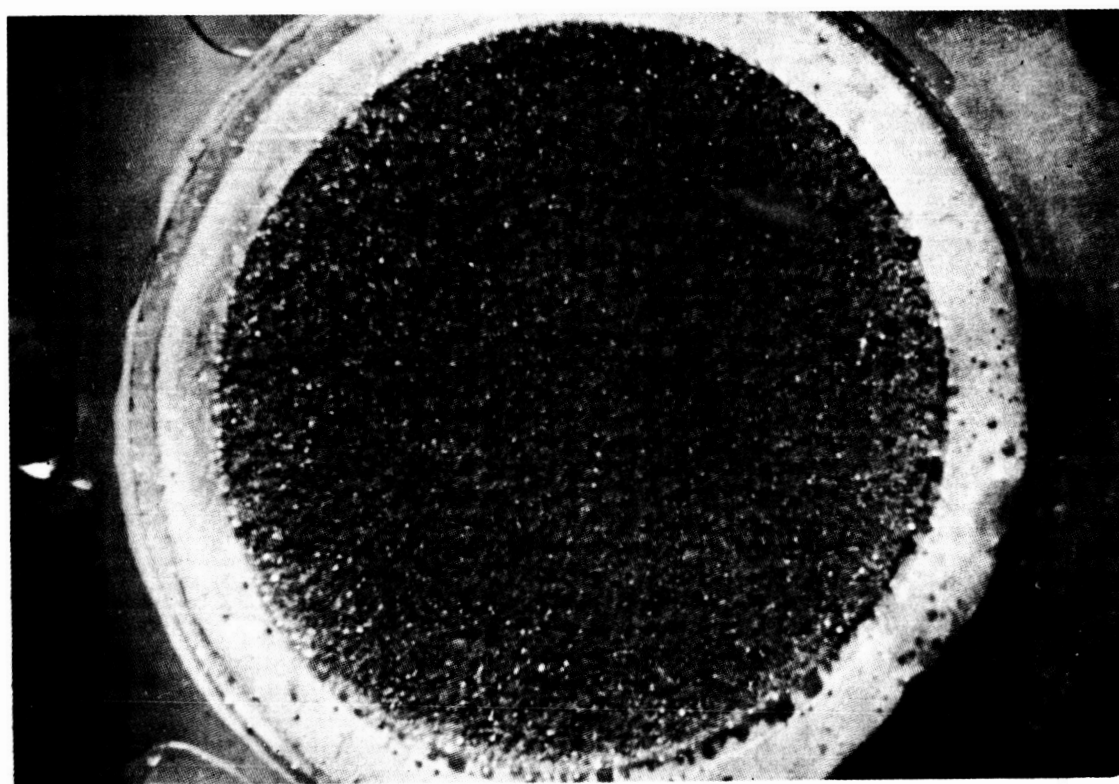
2. 2. 4 Edge Effects

It was demonstrated using the apparatus shown in Figure 1, that preferential propagation of dendrites at the electrode edges can be eliminated. The remedy shown to be effective was to enclose the edges



(Mag. 8X)

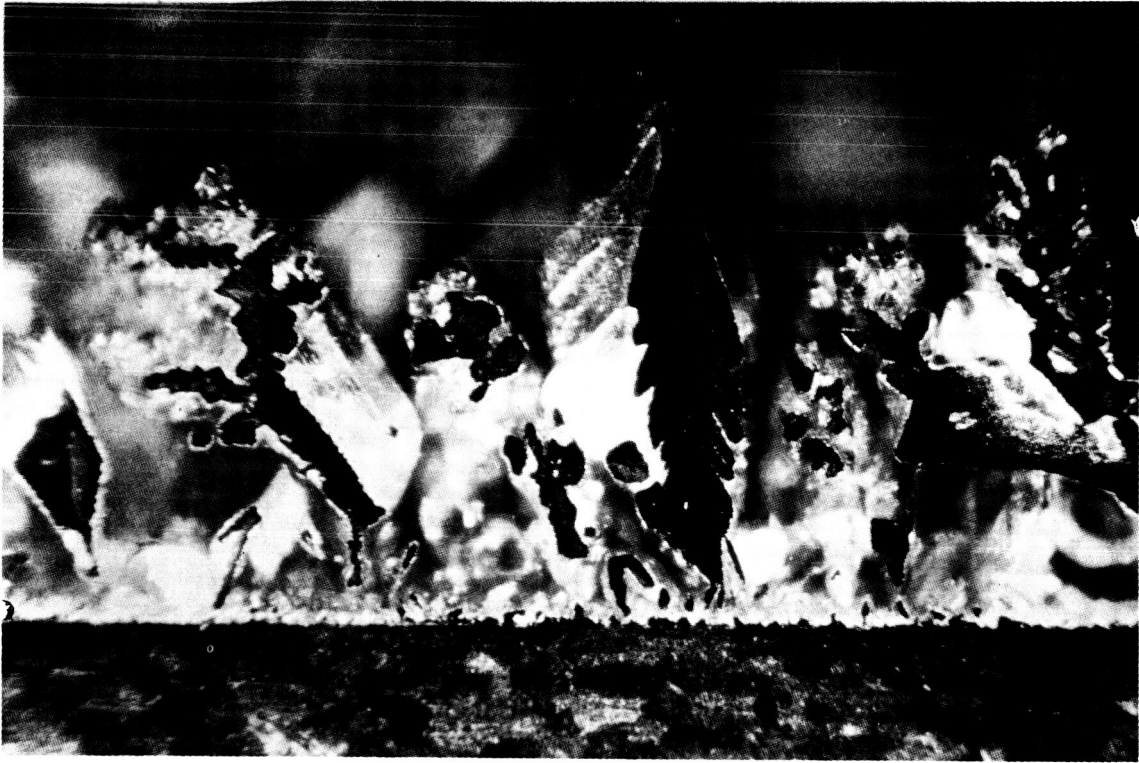
(a) "on" charging



(Mag. 8X)

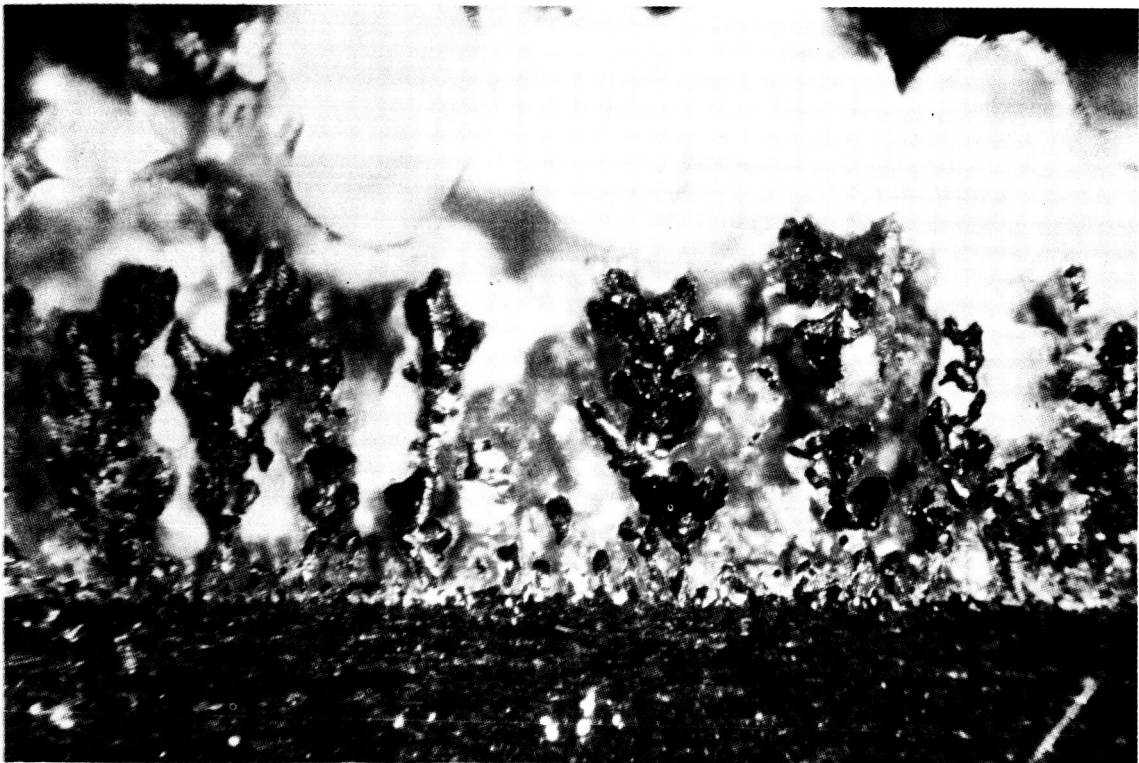
(b) "on/off" charging

Figure 4. Dendrite Growth at -1.8V



(a) "on" charging

(Mag. 100X)



(b) "on/off" charging

(Mag. 100X)

Figure 5. Cross Section Photomicrographs

in an alkali resistant film. This procedure essentially eliminates the possibility of spherical diffusion to the edges. The requirement is only that the thickness of the edge enclosure be of the same dimensions as the expected zinc electrodeposit. This procedure would presumably be equally satisfactory if applied to an actual silver/zinc battery. However, it remains to be seen whether, in a battery, this would eliminate the contribution to preferential edge growth which results from the close proximity of a reservoir of zincate-rich electrolyte at the sides of the electrode stack.

2.2.5 "Single" Dendrite Growth

Using the previously described "edgeless electrode", experiments were conducted to examine the growth of dendrites through cellophane separator material. A piece of cellophane of the type used in commercial silver/zinc batteries was placed above the zinc plate and left for several hours to soak in the electrolyte. A small hole was then made in the cellophane with the tip of a needle and the camera focussed upon it. Experiments were carried out at -1.65 and -1.8 volt versus SCE.

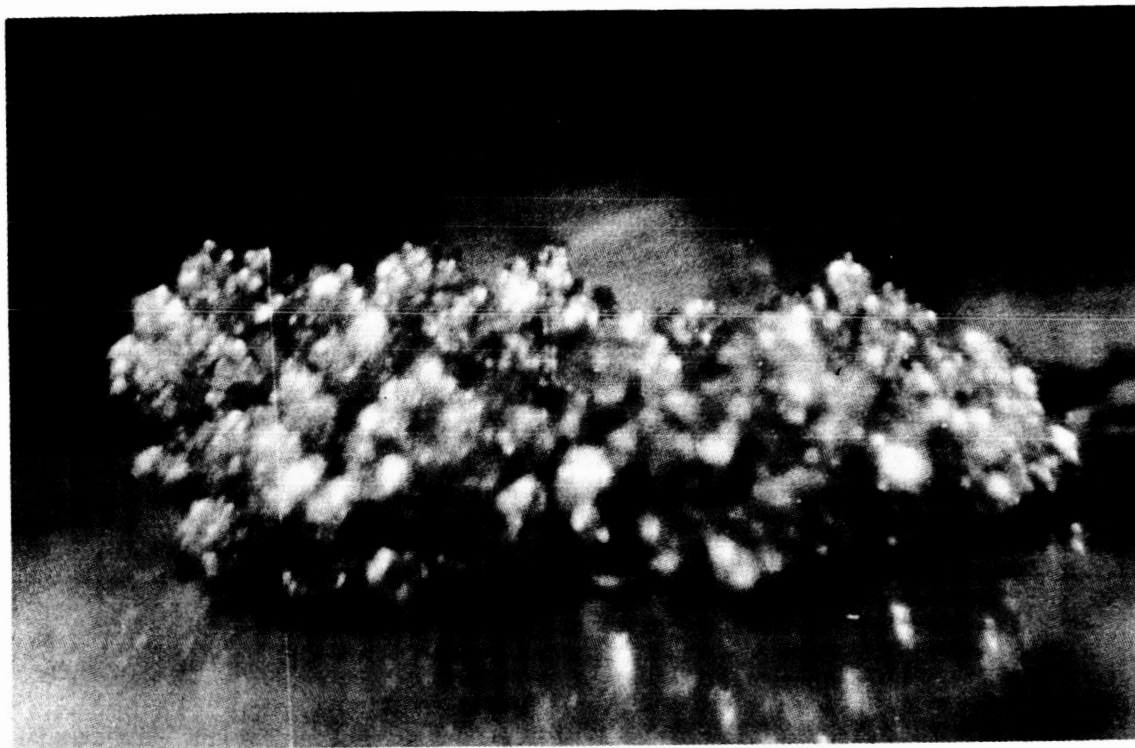
Figures 6(a) and 6(b) are photographs of the growths obtained at -1.65 and -1.8 volt respectively. Two main comments can be made:

- a. The rate of propagation, expressed in mm/minute was seen to be six times greater than is normally observed when a dendrite is grown "en masse"
- b. The morphology shown in both the photographs is typical of deposition at more cathodic potentials. For example, a more mossy growth would be expected at -1.65 volt than was in fact obtained.

Both of these results are felt to emphasize the significance of spherical diffusion. Not only does it lead to higher propagation rates, but in certain instances the morphology is different from that obtained under linear diffusion control.

2.2.6 Dendrite Nucleation and Initiation

No real progress has been made to date in determining what are the factors governing dendrite nucleation. The possibility that nucleation is related to the density of dislocations prompted a study of annealed



(a) -1.65V

(Mag. 100X)



(b) -1.8V

(Mag. 100X)

Figure 6. "Single" Dendrites

and cold-worked substrates. Figures 7(a) and 7(b) are photographs of growths at -1650 mV for cold-worked and annealed samples respectively. The same number of coulombs was passed in each experiment. A tentative conclusion is that on the annealed sample there were less nucleation sites, as judged by the decreased number of dendrite clumps (mossy growth in this case). Further, more basic work is required in this area.

The question also arises as to how early dendrite propagation (initiation) occurs. It is suggested that this results from local convection which is brought about by hydrogen evolution, at any rate in the diffusion-controlled region. This is supported by the capillary diffusion experiments described above. In the purely activation-controlled region, the formation of a mossy growth must be regarded as intrinsic to the system. Further work with the rotating disc electrode (after Yardney) is felt to be important in this area.

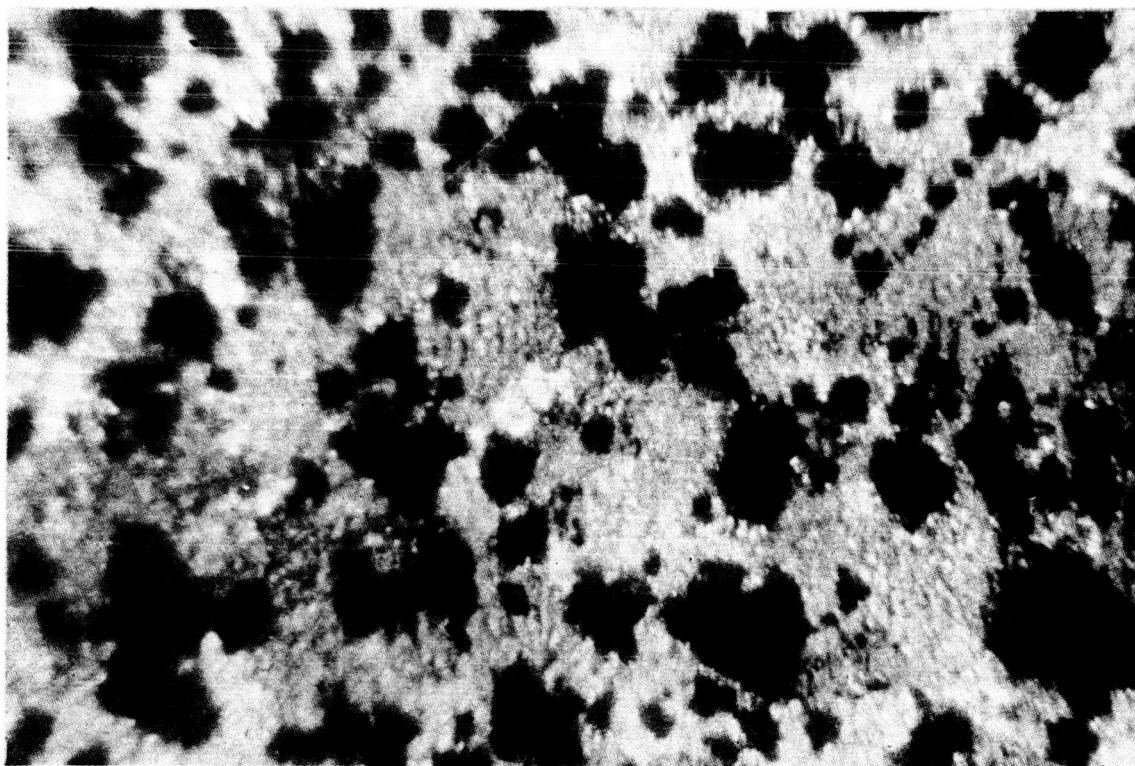
2. 2. 7 Electrodeposition on an Amalgamated Electrode

It has been shown by Lander⁽¹⁸⁾ that an increase in mercury content of the zinc negative electrode leads to a decrease in the cycle life of silver/zinc batteries. This was tentatively ascribed to the growth of zinc particle size and the consequent reduction in surface area. Experiments were conducted using a zinc electrode amalgamated according to the procedure described earlier. The effect was to reduce the rate of growth to some degree but more striking was the effect on the morphology. The crystalline structure of the dendrites tended to be thicker and more individual dendrite propagation was evident as shown in Figure 8. It is therefore not surprising that the cycle life was diminished as reported by Lander since:

- a. there would be more tendency for shorting to occur, and
- b. on discharge the larger dendrites would be harder to remove, which would again increase the likelihood of early failure by shorting.

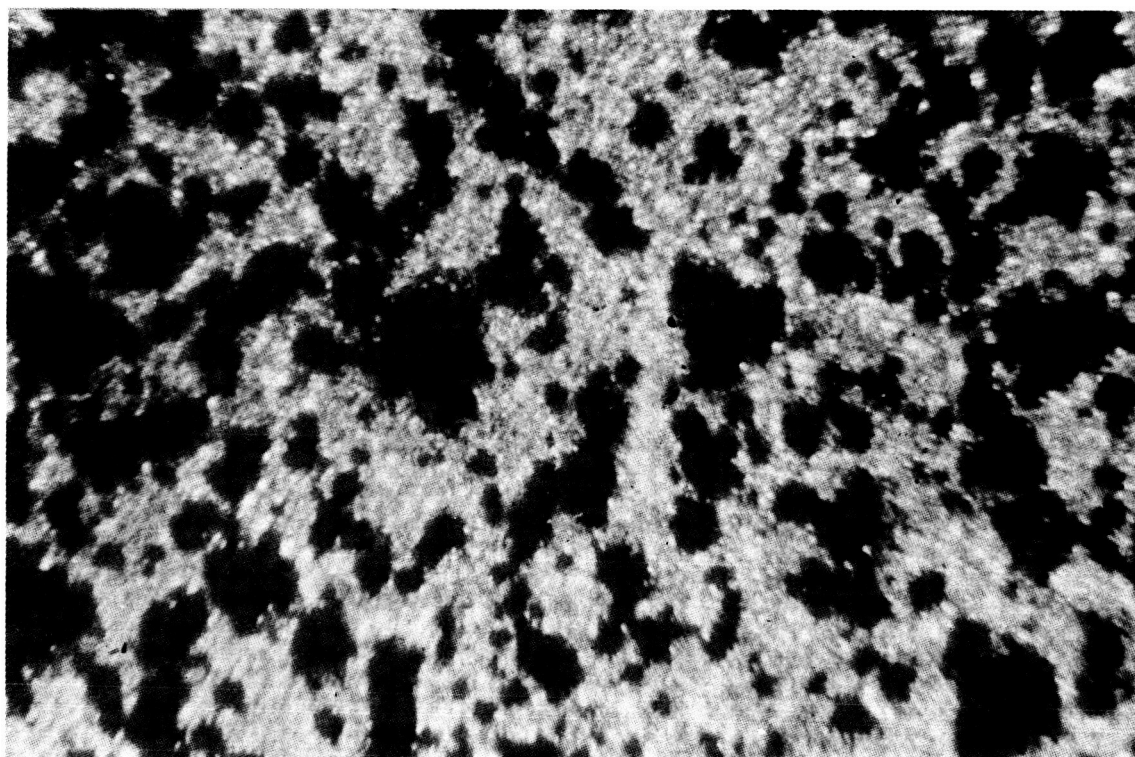
2. 2. 8 Additives

Leveling agents operate by virtue of the fact that they are adsorbed to a greater degree on surface asperities or protrusions and thereby inhibit



(a) annealed

(Mag. 100X)



(b) cold - worked substrate

(Mag. 100X)

Figure 7. Mossy Dendrite Growth at $-1.65V$



(Mag. 100X)

Figure 8. Dendrite Growth on Amalgamated Electrode

growth at these points. There is, however, disagreement concerning the reasons for such preferential adsorption. One theory considers it to be due to energetic differences between peaks and valleys of the irregular surfaces, while the other regards non-uniform adsorption to be governed by concentration polarization: as in the case of the diffusion theory for dendrite propagation, the supply of the dissolved additive will be greatest near the tip due to spherical diffusion; adsorption (and inclusion) will consequently predominate at such a point. Kudryavtsev and co-workers⁽³⁾ have recently presented strong evidence for the validity of the latter hypothesis on the basis of experiments using the rotating disc electrode.

In the present work, the use of additives has been investigated briefly and the materials listed earlier were tested. No firm conclusions can be drawn, however, because only a limited number of experiments were carried out. It did, however, seem that the addition of tin (as Sn^{++}) was beneficial. It is recommended, however, that further work be done and experiments along the lines suggested by Kudryavtsev⁽³⁾ be carried out.

2.2.9 Electrodeposition from Zinc Chloride Solutions

In the second quarterly report, deposition from solutions containing Zn^{++} was discussed. It was suggested that smooth deposits are obtained when zinc is present as the free cation. Some experiments were conducted in the past quarter and it was found that our previous statements (based upon the plating literature) were untrue. Dendrite growth was found to occur. Further, evidence was obtained that the propagation was even more influenced by mass transfer than in the case of alkaline solutions.

SECTION III - NEW TECHNOLOGY

New technology has resulted from this contract relating to:

- a. The use of an edge wrapping technique to prevent the preferential growth of zinc dendrites at the electrode edges, and
- b. The use of an intermittent charging technique to promote the formation of a more dense and even zinc deposit.

The theory and state of development of these two methods are fully described in the body of the report.

SECTION IV - CONCLUSIONS AND RECOMMENDATIONS

The objective of the program was to seek and define specific methods of minimizing the rate of undesirable dendritic growths on the zinc electrode which are responsible for the low reliability of present silver/zinc secondary batteries. The dendritic growths, which form when a discharged or partially discharged zinc plate is recharged, eventually result in metallic bridges between positive and negative plates which short out a parallel stack of plates. To attain this objective, the main effort in this nine-month program was directed towards identifying the factors controlling dendrite growth and defining as far as possible the requirements for preventing or minimizing dendrite formation. Many of the factors have been identified and some requirements for improved electrode electrolyte systems have been defined. Two specific remedies have been proposed, one of which should be investigated in detail to seek an optimum solution.

During the early phase of the contract, at least three distinct dendrite types were observed - mossy, pine-tree and acicular. Many variations of these exist, but they are less readily defined. During the first phase of the program, it was shown that the type of dendrite formed is primarily dependent on the charging overpotential. The mossy dendrites are favored up to overpotentials of 100 mV; pine-tree dendrites in the 100 mV - 200 mV range; and acicular dendrites above 200 mV. The mossy dendrite is a more even and desirable type of growth; the acicular dendrite is the most irregular type and more likely to cause shorting. The mossy dendrites are formed only at low current densities, and this means that zinc plates can only be recharged slowly, thus limiting silver/zinc batteries to low recharging rates.

Experiments were then conducted to determine whether the phenomenon of dendrite growth is dependent on electrode kinetics or mass transfer. Dendrite propagation rate measurements showed that mass transfer of soluble zinc in the electrolyte is a major controlling parameter and that the tip of a dendrite grows because of the slow diffusion rate of zincate ions. Because of this slow diffusion in the liquid phase, the rate of plating out of zinc becomes limited and thus surface protrusions extending beyond the average surface height begin to grow at the expense of low points on the surface. The tips of the dendrites remove most of the zinc from solution and the low points, which are zinc starved, do not grow at the same rate. This process has been called "spherical diffusion" to describe the diffusion paths of zinc which tend to radiate from the dendrite tips.

An important phenomenon which affects limiting mass transfer rates has been discovered and substantiated. This was uncovered after the diffusion coefficient of zincate was determined polarographically as $1.8 \times 10^{-6} \text{ cm}^2/\text{sec}$. Using this value and an arbitrary (but usually the accepted) value of $5 \times 10^{-2} \text{ cm}$. for the diffusion layer thickness, it appeared that the limiting currents observed are an order of magnitude larger than predicted. This difference could not be explained by a high surface roughness factor and it appeared that the diffusion layer thickness must be lower than $5 \times 10^{-2} \text{ cm}$. A series of experiments in which external convection effects were eliminated demonstrated the existence of two intrinsic convection effects occurring on the zinc surface as a direct result of the electrode processes. H_2 bubble formation (on a very small scale) would appear to be one source of convection; the second convection effect is caused by density differences between zinc-saturated and zinc-depleted KOH. These convection effects are very localized (in the region of the dendrite tips) and may be enhancing the rate of dendrite propagation. They cannot be considered as major stirring effects which would, of course, increase mass transfer in the bulk electrolyte and result in very high Reynold's numbers, within the zinc matrix. This phenomenon has not been previously discussed in the literature, but may have significance in other electrode processes.

Investigation of amalgamated electrodes (porous, up to 4% Hg) showed that amalgamation has little effect on the type of dendrite formed in the potential regions listed above.

An extremely important effect was observed at the edge of flat electrodes during charge. It was observed that dendrite propagation was enhanced at the edge of the electrodes: this would lead to bridging along the edge of a stack. A remedy has been proposed to eliminate this effect which is caused by "spherical diffusion" of zincate to the edge of the electrode.

It is proposed that the negative plate edges should be sealed with a non-porous plastic (polyethylene) forming a ridge which projects above the zinc surface preventing enhanced diffusion to the edge of the plate.

Further consideration of the zincate mass-transfer limitations and localized convection effects indicated the possibility of controlling dendrite growth by modified charging technique. Only a few preliminary experiments were within the scope of this program, but, using 30% "on" 60% "off" charging cycle at constant potential, the dendrite growth was less marked than in the case of 100% "on" charging at the same potential.

Some preliminary studies of electrolyte additives which were used in the expectation that selective adsorption on cathodic sites might lessen dendrite propagation rates showed no observable effect. Although it is recommended that further studies of this approach be carried out, the absence of any effect perhaps emphasizes the overriding importance of mass-transfer control.

In view of the progress made during this nine-month study in identifying controlling parameter, it is recommended that the work be continued to develop a more detailed knowledge of dendrite growth and to demonstrate the efficiency of proposed modifications to the system.

In particular, the following areas should receive attention:

- a. Manufacture of edge-protected electrodes and observations of this modification in the uniformity of dendrite growth during repeated charge/discharge cycles.
- b. Experimental and paper study of the possibilities of intermittent charging (interrupted D.C.) and superimposed A.C./D.C. techniques. The objective of this approach is to speed up mass-transfer to the low-points on the surface. An effective solution, of course, must aim at the same integrated charging rate; otherwise, the same effect can be achieved obviously by working at a lower current density.
- c. Develop a theory or theories for the nucleation and initiation of dendrites. The success of such a task is difficult to predict. An attempt should be made to analyze the control (if any) exerted by: (1) different surfaces, e.g., Cu and Ni and other high hydrogen over-voltage metals, and (2) variations in solution composition.
- d. Develop a more advanced theory for the discharge step, $\text{Zn(OH)}\frac{5}{4} + 2\text{e}^- \longrightarrow \text{Zn} + 4\text{OH}^-$. It is very difficult to study the kinetics of this process at a solid electrode because of the constantly changing area associated with dendrite formation. Consideration should therefore be given to: (1) the use of a mercury electrode, and (2) the use of a rotating electrode. The reaction should also be studied at low KOH concentrations where the $\text{Zn(OH)}\frac{3}{2}$ species predominates. (18)
- e. Develop a theoretical understanding of the role of additives as leveling agents. A further attempt should be made to examine the role of additives in the present system.

- g. Analyze the importance of temperature in the range 0 - 50°C. The effect of temperature has not as yet been included in our work. It was, however, mentioned in the work of Kryukova (loc. cit.) that the effect of raising the temperature was to diminish dendrite propagation. This could be ascribed on the basis of our present theories to the higher diffusion rate which would result therefrom.

The need for work in these areas is demonstrated in this final and the preceding quarterly report. We believe that work along these lines will lead to an improvement in zinc electrode life.

APPENDIX

The main reactions associated with the silver/zinc alkaline battery and their relative positions in the electrochemical series of potential are summarized in Figure A-1. Potentials refer to standard state conditions and are quoted with reference to the standard saturated calomel electrode (SCE). Included on this diagram are the potentials corresponding to (a) passivation of the zinc electrode, and (b) the formation of different morphological varieties of zinc.

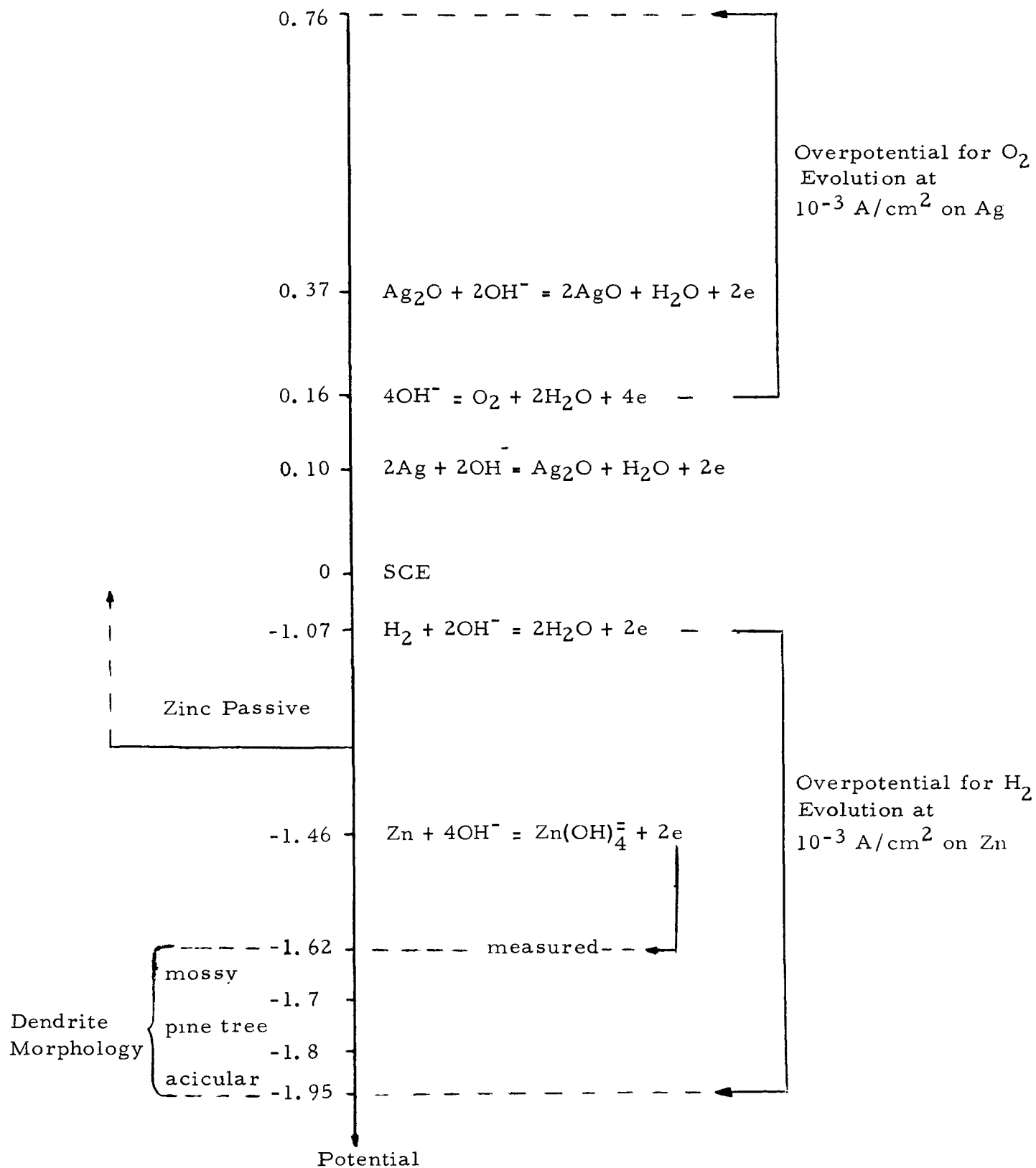


Figure A-1. Potential Series for Silver/Zinc Battery

REFERENCES

1. J. E. Cooper and A. Fleischer, Eds., Characteristics of Separators for Alkaline Silver Oxide/Zinc Secondary Batteries, Aero Propulsion Laboratory, Wright-Patterson AFB, Ohio.
2. T. W. Higgins and P. F. Bruins, Extended Abstract Number 41, Electrochemical Society Meeting, New York (1963).
3. T. A. Kryukova in Soviet Electrochemistry, Vol. III, p 147f, Consultants Bureau, N. Y. (1961).
4. S. S. Kruglikov, N. T. Kudryavtsev, G. F. Vorobiova, and A. Ya. Antonov, Electrochim. Acta, 10, 253 (1965).
5. V. V. Romanov, Zhur. Priklad. Khim., 36 (5), 1050 (1963).
6. V. V. Romanov, U. S. S. R. Patent No. 141,187 (1961).
7. V. V. Romanov, Zhur. Priklad. Khim., 35, 1293 (1962).
8. N. T. Kudryavtsev and A. I. Lysovelskova, Vestnik Inzhenerov. Tekh., 183 (1947).
9. N. T. Kudryavtsev and A. A. Nikiforova, U. S. S. R. Patent No. 57,509 (July 31, 1940).
10. N. T. Kudryavtsev and G. A. Subova, Karroziya i Borba s Nei, 7, No. 2, 27 (1941).
11. J. L. Barton and J. O'M. Bockris, Proc. Roy. Soc., A268, 485 (1962).
12. See P. Delahay, New Instrument Methods in Electrochemistry, Chapter 9, Interscience, New York (1954).
13. G. Wranglen, Electrochim. Acta, 2, 130 (1960).
14. Yardney Electric Corporation, Contract Number NAS 5-3873, 1st Quarterly Report (1964).
15. H. A. Laitinen and I. M. Kolthoff, J. Amer. Chem. Soc., 61, 3344 (1939).

16. H. A. Laitinen and L. M. Kolthoff, J. Amer. Chem. Soc., 61, 3344 (1939).
17. J. J. Lingane, Ind. Eng. Chem., Anal. Ed., 15, 583 (1943).
18. J. J. Lander, Third Biennial Aerospace Power Systems Conference (AIAA), Paper No. 64-749, Sept. 1964.
19. T. P. Dirkse, C. Postmus, and R. Vandenbosche, J. Amer. Chem. Soc., 76, 6022 (1954).